metal-organic compounds

A new polymorph, form *C*, of [1,2-bis(diphenylphosphino)ethane]-dichloronickel(II)

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The title compound, $[NiCl_2(C_{26}H_{24}P_2)]$, has arisen as a result of the unexpected reduction (hydrogenation) of the *trans*-1,2-bis(diphenylphosphino)ethene ligand. The hydrothermal reaction conditions have produced a third polymorphic form of the compound which has twofold symmetry, crystallizes in an enantiomer-selective manner and contains an unexpectedly short C—C (ethane) bond. Contacts of the form C—H···Cl are present, one involving alkyl and the other aryl hydrogen, with C···Cl distances of 3.556 (4) and 3.664 (6) Å, respectively.

Comment

The Cambridge Structural Database (CSD; Allen & Kennard, 1993), accessed at the Chemical Database Service of the EPSRC (Fletcher *et al.*, 1996), provides three reports of structures for the title compound. Spek *et al.* (1987) reported the structure of the dichloromethane solvate (FUJXUD) which was subsequently re-examined by Busby *et al.* (1993) and designated form *B* along with a second unsolvated structure (form *A*, PIFDUD). The structure of form *A* was later determined with greater precision (PIFDUD01; Davies *et al.*, 1998). Following the notation of Busby *et al.* (1993), we designate the polymorph described here as form *C*. In the following discussion the various structures (polymorphs) are designated simply by letter as *A*, *B* or *C* and in addition the 150 and 293 K structures presented here are further differentiated as *A*(150), *C*(150) and *C*(293).
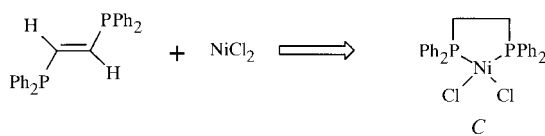
The molecules of *C* (Fig. 1) contain a twofold crystallographic symmetry axis passing through Ni and the midpoint of the C1—C1^i bond [symmetry code: (i) $-x, y, -z$]. Thus, in addition to Ni in the 2*a* special positions of the space group *I*2,

the asymmetric unit consists of one Cl and half of the ligand comprising P, the ethane C1, and C2–C13 of the phenyl groups attached to P. The latter are in the 4*b* general positions. According to Busby *et al.* (1993), molecules of *B* possess similar but non-crystallographic twofold axial symmetry, while those of *A* do not due to the disposition of the phenyl groups. In all of the polymorphs, the coordination of Ni remains essentially similar, in the form of a slight tetrahedral distortion from a square-planar arrangement.

Solely on the basis of the mode of preparation of *C* (see below), it was assumed initially that in forming the complex *C* the original *trans*-substituted diphosphinoalkene had simply undergone transformation to the *cis* form. However, the length of the putative C=C bond provoked investigation of a model with two rather than one H atom attached to C1 resulting in a small but significant improvement in the *R* factor. The correctness of this model was confirmed by ^{1}H NMR and supported by elemental analysis and the discovery of crystals of *A* in admixture with *C*, one of which was used to provide intensity data at 150 K [*A*(150)] whose analysis is presented here merely for comparison purposes (Fig. 2 and Table 1).

It follows that in the synthesis of *C*, accompanied by some *A*, by the method described below, the initial phosphine disubstituted alkene ligand has undergone hydrogenation. This is comparable with the dihalobis(triphenylphosphine)-nickel(II)-catalysed hydrogenation of methyl linoleate with tetrahydrofuran as the hydrogen source (Itatani & Bailar, 1967) supported by the detailed investigation of the generation of H_2 in a similar system as reported by Davies *et al.* (1998).

In the scheme, molecules of *A*, *B* and *C* are handed because, relative to the immediate coordination of Ni with Cl down below the plane of the paper (small rectangles), the C—C ethane bond of the ligand may be either rotated clockwise, (i), or anticlockwise, (ii). Centrosymmetric *A* and *B* are racemic in this respect but *C* is not. By coincidence, the molecules of *C*(293) correspond to (i) and those of *C*(150), with a second crystal, to (ii).

Table 1 shows that the molecules of *A*, *B* and *C* are very similar, except that the ethane C—C of the ligand is approximately 0.1 Å shorter in *C* than in *A* or *B*. The dihedral angles around this bond, while of opposite sign for the enantiomers *C*(293) and *C*(150), are smaller in magnitude than the corresponding values in *A* or *B*.

Short C—C bonds in ligands of this type are by no means uncommon and extreme cases are, for example, values of 1.380 (10) Å in *trans*-bis[1,2-bis(dimethylphosphino)ethane]-*P*,*P*′-dichlorochromium(II) (DAJDUN; Girolami *et al.*, 1985) or 1.326 (10) Å in dichlorobis[1,2-bis(dimethylphosphino)-ethane]iron(II) (BAWSOH; di Vaira *et al.*, 1981), and are usually accounted for by disorder or extreme thermal displa-
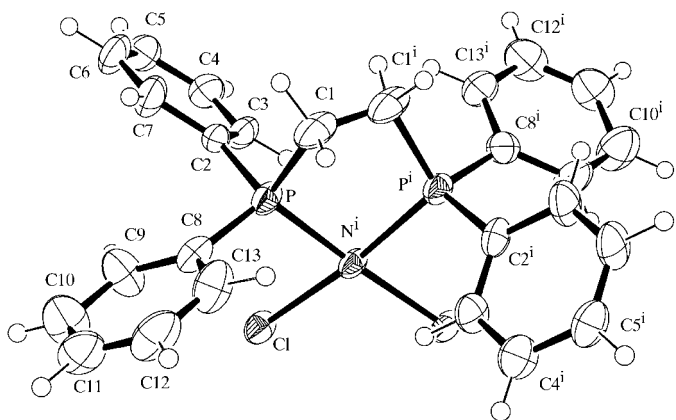
Figure 1
A molecule of C showing the atom-labelling scheme. Selected symmetry-related [symmetry code: (i) $-x$, y, $-z$] atoms are labelled. Non-H atoms are shown as 50% probability ellipsoids and H atoms are shown as open circles.

cement or a combination of both. However, in the case of C, the complete success of the refinement of the absolute structure in both instances with no evidence of twinning or any other form of disorder leaves the shortness of the ethane C—C bond still to be accounted for by other means. Decrease in the temperature of data collection from 293 to 150 K has no effect on this C—C bond length in A but causes an increase in length by about 1% in C. This can be attributed to libration in the case of C but the change is small compared with the overall discrepancy between C and A or B. There is, however, one feature in the structure of C which is totally absent in A or B. This is the hydrogen-bond type contact of the form C1—H1A···Cl present in Fig. 3 and Tables 2 and 3, which interconnects the molecules in columns propagated in the direction of the polar b axis. In this arrangement, Cl donates electron density to the alkyl H atom, which is then presumed to release
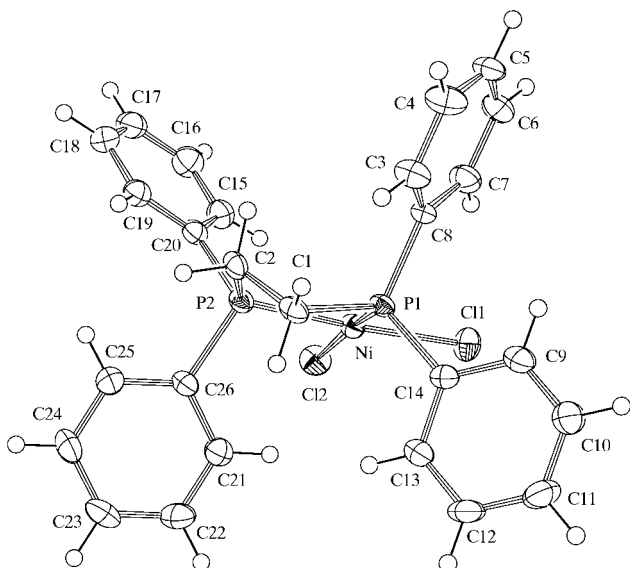
electron density to the C atom to which it is attached, thus imparting some double-bond character to the C—C bond and thus shortening it. If this is the case, the effect is surprisingly large. There is also present in C an aryl H contact of the form C12—H12···Cl which serves to interconnect the columns of molecules in sheets parallel to ($\bar{1}$01). Both of these contacts were elucidated by means of *PLATON* (Spek, 1990).
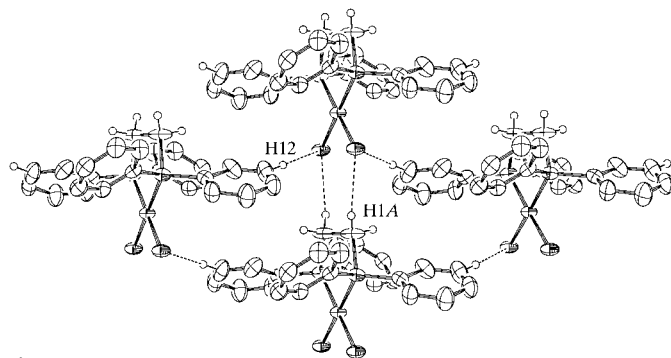
Figure 3
Part of a layer parallel to ($\bar{1}$01), which is also the plane of projection, of C—H···Cl-connected (dashed lines) molecules of C. The cell edge b runs down the page and, aside from the omission of aryl H atoms not involved in hydrogen-bond formation, the representation is the same as in the other figures.

Experimental

trans-1,2-Bis(diphenylphosphino)ethene (114 mg, 0.288 mmol), nickel chloride hexahydrate (68 mg, 0.286 mmol) and ethanol (10 ml) were placed in a 23 ml Parr bomb. After sealing, the bomb was heated at 100 K h^{-1} to 423 K and maintained at this temperature for 48 h. Thereafter the bomb was cooled to 293 K at a rate of 5 K h^{-1}. After opening, the brown–yellow crystals were collected by filtration, washed with ethanol and air dried to afford C as an analytically pure solid. Found: C 59.1, H 4.5% ($C_{26}H_{24}Cl_2NiP_2$ requires C 59.2, H 4.6%). IR (KBr): 1638 (m), 1618 (m), 1476 (w), 1433 (s), 1406 (w), 1385 (w), 1306 (w), 1274 (w), 1186 (w), 1160 (w), 1129 (w), 1102)s), 1069 (sh), 1025 (w), 997 (w), 875 (w), 847 (w), 813 (m), 782 (w), 748 (s), 717 (s), 704 (m), 689 (s), and 652 (w) (cm^{-1}). ^{1}H NMR (250 MHz, CDCl$_3$): δH 8.0 (m) and 7.5 (m, 20H), and 2.1 (m, 4H); *cf.* footnote a in Table 1 of Davies *et al.* (1998).

Compound *C*(150)

Crystal data

[NiCl$_2$(C$_{26}$H$_{24}$P$_2$)]	$D_x = 1.406$ Mg m^{-3}
$M_r = 528.0$	Mo $K\alpha$ radiation
Monoclinic, $I2$	Cell parameters from 5686
$a = 12.4551$ (14) Å	reflections
$b = 7.9901$ (8) Å	$\theta = 3.0$–27.5°
$c = 13.0350$ (19) Å	$\mu = 1.13$ mm^{-1}
$\beta = 105.983$ (5)°	$T = 150$ (2) K
$V = 1247.1$ (3) Å^3	Needle, brown–yellow
$Z = 2$	$0.20 \times 0.03 \times 0.03$ mm

Data collection

KappaCCD diffractometer	1946 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.064$
Absorption correction: multi-scan	$\theta_{\text{max}} = 27.5°$
(*SORTAV*; Blessing, 1995, 1997)	$h = -15 \rightarrow 12$
$T_{\text{min}} = 0.887$, $T_{\text{max}} = 0.999$	$k = -8 \rightarrow 10$
5686 measured reflections	$l = -13 \rightarrow 16$
2686 independent reflections	Intensity decay: none

Figure 2
A molecule of A(150) showing the atom-labelling scheme. The representation is the same as that of Fig. 1.

metal-organic compounds

Table 1
Selected bond lengths and angles (Å, °) for A, B and C.

	A	A'	$A(150)$	B	$C(293)$	$C(150)$
Ni—Cl	2.199 (2)	2.1990 (6)	2.2002 (4)	2.2003 (11)	2.1999 (14)	2.0254 (13)
Ni—P	2.154 (2)	2.1524 (6)	2.1493 (5)	2.1507 (11)	2.1340 (15)	2.1346 (13)
P—C1	1.837 (5)	1.832 (2)	1.8340 (14)	1.834 (4)	1.833 (4)	1.836 (4)
P—C2	1.814 (4)	1.820 (2)	1.8200 (14)	1.808 (3)	1.800 (4)	1.800 (4)
P—C8	1.818 (4)	1.816 (2)	1.8150 (14)	1.811 (3)	1.792 (6)	1.804 (4)
C1—C1$^\mathrm{i}$	1.516 (11)	1.508 (3)	1.515 (3)	1.523 (7)	1.400 (11)	1.413 (10)
Ni—P—C1	108.3 (2)	108.33 (6)	108.54 (6)	109.27 (12)	108.68 (15)	108.77 (16)
Ni—P—C2	113.34 (13)	113.50 (6)	113.19 (6)	110.98 (12)	112.12 (19)	111.42 (17)
Ni—P—C8	116.66 (13)	116.81 (6)	116.61 (6)	119.43 (12)	116.12 (16)	116.05 (15)
Cl—Ni—Cl$^\mathrm{i}$	94.60 (9)	94.59 (3)	94.69 (3)	95.47 (4)	96.51 (8)	97.45 (7)
Cl—Ni—P	89.29 (6)	89.32 (3)	89.36 (2)	88.84 (4)	88.13 (4)	87.78 (4)
Cl—Ni—P$^\mathrm{i}$	173.18 (8)	173.13 (3)	172.98 (2)	175.12 (5)	174.60 (7)	173.87 (6)
P—Ni—P$^\mathrm{i}$	87.24 (10)	87.18 (3)	86.99 (2)	86.93 (4)	87.38 (8)	87.18 (7)
C1—P—C2	103.8 (2)	104.00 (9)	104.03 (8)	104.85 (14)	105.5 (3)	105.9 (2)
C1—P—C8	104.5 (2)	104.71 (8)	104.30 (8)	104.80 (14)	105.7 (3)	106.0 (2)
C2—P—C8	109.0 (2)	108.30 (8)	108.98 (8)	106.35 (14)	108.0 (2)	108.1 (2)
P—C1—C1$^\mathrm{i}$	106.8 (3)	107.08 (14)	106.56 (11)	107.0 (2)	110.7 (3)	109.9 (3)
P—C1—C1$^\mathrm{i}$—P$^\mathrm{i}$	49.6 (6)	49.3 (2)	49.90 (18)	47.8 (4)	40.6 (8)	−42.7 (6)

Notes: the bond and angle designations are those appropriate for the symmetric molecules of C [symmetry code: (i) $-x, y, -z$] and therefore data for A (PIFDUD; Busby *et al.*, 1993), A' (PIFDUD01; Davies *et al.*, 1998), $A(150)$ (this work) and B (FUJXUD; Spek *et al.*, 1987) are for the most part given as pairwise mean values with s.u.'s adjusted accordingly. For all except $A(150)$, $C(293)$ and $C(150)$, *PLATON* (Spek, 1990) was used to compute distances and angles from CIF data from the CSD.

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0296P)^2 + 0.0327P]$
$R[F^2 > 2\sigma(F^2)] = 0.050$	
$wR(F^2) = 0.105$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
2686 reflections	$\Delta\rho_{max} = 0.54$ e Å^{-3}
141 parameters	$\Delta\rho_{min} = -0.58$ e Å^{-3}
H-atom parameters constrained	Absolute structure: Flack (1983)
	Flack parameter = 0.01 (2)

Table 2
Hydrogen-bonding geometry (Å, °) for $C(150)$.

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1A···Cl$^\mathrm{i}$	0.99	2.69	3.556 (4)	147
C12—H12···Cl$^\mathrm{ii}$	0.95	2.74	3.664 (6)	166

Symmetry codes: (i) $x, y-1, z$; (ii) $-\frac{1}{2}-x, y-\frac{1}{2}, -\frac{1}{2}-z$.

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o{}^2) + (0.0223P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.049$	where $P = (F_o{}^2 + 2F_c{}^2)/3$
$wR(F^2) = 0.100$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.95$	$\Delta\rho_{max} = 0.27$ e Å^{-3}
2861 reflections	$\Delta\rho_{min} = -0.34$ e Å^{-3}
141 parameters	Absolute structure: Flack (1983)
H-atom parameters constrained	Flack parameter = 0.01 (2)

Table 3
Hydrogen-bonding geometry (Å, °) for $C(293)$.

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1A···Cl$^\mathrm{i}$	0.97	2.73	3.570 (4)	145
C12—H12···Cl$^\mathrm{ii}$	0.93	2.80	3.714 (8)	168

Symmetry codes: (i) $x, 1+y, z$; (ii) $-\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{2}-z$.

Compound $C(293)$

Crystal data

[NiCl$_2$(C$_{26}$H$_{24}$P$_2$)]	$D_x = 1.379$ Mg m^{-3}
$M_r = 528.0$	Mo $K\alpha$ radiation
Monoclinic, $I2$	Cell parameters from 4976
$a = 12.5688$ (15) Å	reflections
$b = 8.0208$ (8) Å	$\theta = 3.0$–30.1°
$c = 13.0871$ (9) Å	$\mu = 1.11$ mm^{-1}
$\beta = 105.531$ (4)°	$T = 293$ (2) K
$V = 1271.2$ (2) Å^3	Needle, brown–yellow
$Z = 2$	$0.35 \times 0.07 \times 0.05$ mm

Data collection

KappaCCD diffractometer	1576 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.050$
Absorption correction: multi-scan	$\theta_{max} = 30.1°$
(*SORTAV*; Blessing, 1995, 1997)	$h = -16 \rightarrow 13$
$T_{min} = 0.896$, $T_{max} = 0.955$	$k = -10 \rightarrow 8$
4976 measured reflections	$l = -15 \rightarrow 16$
2861 independent reflections	Intensity decay: none

Compound $A(150)$

Crystal data

[NiCl$_2$(C$_{26}$H$_{24}$P$_2$)]	$D_x = 1.486$ Mg m^{-3}
$M_r = 528.0$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 20 644
$a = 11.2779$ (3) Å	reflections
$b = 13.3386$ (4) Å	$\theta = 2.9$–27.5°
$c = 15.8739$ (5) Å	$\mu = 1.20$ mm^{-1}
$\beta = 98.7953$ (16)°	$T = 150$ (2) K
$V = 2359.85$ (12) Å^3	Block, brown–yellow
$Z = 4$	$0.20 \times 0.15 \times 0.10$ mm

Data collection

KappaCCD diffractometer	4070 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.042$
Absorption correction: multi-scan	$\theta_{max} = 27.5°$
(*SORTAV*; Blessing, 1995, 1997)	$h = -14 \rightarrow 14$
$T_{min} = 0.659$, $T_{max} = 0.887$	$k = -16 \rightarrow 17$
9650 measured reflections	$l = -17 \rightarrow 20$
5198 independent reflections	Intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0671P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.042$	$+ 0.0545P]$
$wR(F^2) = 0.117$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
5198 reflections	$\Delta\rho_{max} = 0.71$ e Å^{-3}
280 parameters	$\Delta\rho_{min} = -0.54$ e Å^{-3}
H-atom parameters constrained	

The room-temperature structure of *C* was solved initially by simply extracting feasible positions for non-H atoms from a difference map phased by placing Ni at the origin of the space group *I*2/*m*. This readily produced an image of a pair of superimposed molecules and it was comparatively easy to select one of these and continue refinement in the true space group (*I*2). The coordinates thus derived were used along with appropriately modified cell dimensions as starting parameters for the refinement of the 150 K structure of *C*. Starting parameters for the refinement of *A*(150) were likewise taken from the literature data (PIFDUD; Busby *et al.*, 1993). In all three refinements, H atoms were placed in calculated positions and refined riding with $U_{iso} = 1.2U_{eq}$ of the C atoms to which they were attached. The absolute structures of *C*(150) and *C*(293) are based on 1170 and 1187 Friedel pairs, respectively.

For all compounds, data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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